NASA TECH BRIEF

Quantum Mechanical Calculations of Reactive Scattering Cross Sections in Bimolecular Encounters

Theoretical treatments of gas phase chemical reactions can be conveniently classified into two parts. The first involves the study of the details of intermolecular or intramolecular energy transfer, particle exchange, particle emission, or particle capture. Secondly, a study must be made of the manner in which a usually broad spectrum of the above microscopic processes are reflected in the macroscopic or bulk behavior of gas phase reactions. Thus, the first task is concerned with the calculation of the probability of particular events, while the second is concerned with formalizing mathematical relationships between these detailed probabilities and observable reaction phenomena.

A study has been made that is involved with the application of the nonequilibrium collision theory of reaction rates to the estimation of rate constants for simple reactions. In the nonequilibrium collision theory, the molecular collisions are individually studied with regard to initial conditions, particle exchange, and energy exchange, the results being defined in terms of cross sections. Then, the kinetic theory of gases is used to average over all the effects of the individual collisions resulting in reactions to obtain the rate constants.

The following conclusions were reached in this study:

The investigation demonstrated the severe complications encountered in the quantum mechanical description of chemical reactions. Even the relatively simple derivation of an expression for the reaction cross section involved tedious attention to detail. Furthermore, the subsequent calculation of the reaction cross section required so much computer time, even on a high speed computer, that computations were limited to a few representative initial conditions.

It was shown that good agreement between theory and experiment can be obtained if sufficient care is taken in approximating the exact wave function for the collision. Using the perturbed Morse oscillator method to describe the distortion of the HBr bond in the presence of another bromine atom resulted in reaction cross sections which, when used in a simplified collision theory, gave rate constants that compared favorably with experiment.

Detailed rate constant calculations by the perturbed Morse oscillator method reinforce the classical mechanical results of Polanyi. That is, "attractive" potential energy surfaces lead to higher vibrational states for the products, whereas "repulsive" potential energy surfaces result in less vibration of the product molecule. Since infrared chemiluminescence spectroscopy has demonstrated that the product molecules in the reaction $H + Br_2 \rightarrow HBr + Br$ are formed predominantly in the lower vibrational states, it is concluded that the potential energy surface for the reaction is "repulsive." The exact degree of repulsiveness has not yet been accurately determined.

Notes:

1. This thesis was presented to the faculty of the graduate division of the Georgia Institute of Technology in partial fulfillment of the requirements for the degree of doctor of philosophy in the School of Chemical Engineering, April 1967.
2. Inquiries concerning this study may be directed to:

   Technology Utilization Officer
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   Reference: B67-10527

(continued overleaf)

Patent status:

Inquiries about obtaining rights for the commercial use of this invention may be made to NASA, Code GP, Washington, D.C. 20546.

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